Modeling Polyethylene-Solvent Mixtures with the Sanchez-Lacombe Equation

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Abstract

The Sanchez-Lacombe equation of state was used to model cloud-point isotherms of two systems of polyethylene in ethylene and in one system of polyethylene in n-hexane. The three polyethylene samples examined were very dissimilar in average molar mass and polydispersity. Alternative solvent parameter sets were considered. Polymer parameters were obtained by fitting pure polyethylene volumetric data using an additional volume shift coefficient. Excellent agreement with the experimental cloud point data could be achieved for all three systems mentioned above. Henry's constants for ethylene in polyethylene were also well matched by the same parameter sets.

Introduction

The Sanchez-Lacombe equation of state [1, 2] is one of the simpler models that is capable of at least qualitative correlation of polyethylene-solvent phase behavior. Our intention was to examine whether a single set of parameters for polyethylene could be employed to obtain useful correlations for polyethylenes of varying character and with different solvents. The data examined are two sets of the extensive measurements by de Loos [3, 4], with ethylene as the solvent, and the data of Kennis [5,6] with n-hexane. One of the de Loos polymers was moderately polydisperse and the other was almost monodisperse. The polyethylene Kennis studied had a very high polydispersity.

Sanchez-Lacombe Parameters

The Sanchez-Lacombe equation [1, 2] was used in the form reported by Koak and Heidemann [7]

$$p = \frac{RT(1-d)}{v} - \frac{RTd^2}{b} \ln\left(\frac{v - b/d}{v}\right) - \frac{a}{v^2} \tag{1}$$

where, for mixtures,

$$a = \sum_{i=1}^{nc}\sum_{j=1}^{nc} x_i x_j d_i d_j (1 - k_{ij})\sqrt{\varepsilon_i \varepsilon_j}\, \frac{\left(v_i^* + v_j^*\right)}{2} \tag{2}$$

$$b = \sum_{i=1}^{nc}\sum_{j=1}^{nc} x_i x_j d_i d_j\, \frac{\left(v_i^* + v_j^*\right)}{2} \tag{3}$$

and,
$$d = \sum_{i=1}^{nc} x_i d_i \tag{4}$$

There are three pure component parameters, v_j^*, d_j and ε_j, with d_j made proportional to the molar mass of a polymer component. There is one binary parameter per pair, k_{ij}.

Polyethylene

Sanchez and Lacombe [8] regressed parameters in their equation of state for a number of substances and for a number of polymers. The polyethylene parameters were fitted to reference pressure-temperature-volume data of Olabisi and Simha [9]. Critical properties and vapor pressures, which are used to obtain parameters in the cubic equations of state hold little or no relevance to polymer behavior.

In most applications of the cubic equations of state, accurate vapor pressures are the major concern and precise liquid densities are not. However, Peneloux et al. [10] showed that liquid densities might be improved by adding a "volume shift" parameter to the equations. Mechanically, the improvement is obtained by adding a possibly temperature dependent constant to the volume calculated from the original equation of state. In mixtures, the equation is;

$$v^{shift} = v + \sum_i x_i c_i = v + c \tag{5}$$

The relationships between the original thermodynamic functions and those that are shifted are;

Helmholtz free energy; $\qquad A^{shift} = A(T, V + nc, n_1, \cdots, n_c) \tag{6}$

Pressure; $\qquad P^{shift} = P(T, V + nc) \tag{7}$

Chemical potential; $\qquad \mu_i^{shift} = \mu_i + c_i P \tag{8}$

The principal attractiveness of this idea is that phase equilibria calculated from the original equations are not modified by the volume shift, since chemical potentials equal in the original phases remain equal after volume shifting [10,11].

We have fitted a volume shifted version of the Sanchez-Lacombe equation to the polyethylene reference data using a non-linear least-squares fitting procedure to minimize the objective function;

$$R = \sum_{j}^{ndata} \left(P - P_{\exp_j} \right)^2 \tag{9}$$

The four parameters found in this way are highly correlated and we have found a series of parameters, all of which give virtually equivalent fits to the volumetric behavior. The process we used was to fix the Sanchez-Lacombe energy parameter, ε, and to minimize the objective function with respect to the remaining three parameters, including the volume shift parameter. The results are given in Table 1. The parameters fitted by Sanchez and Lacombe, without the volume shift, are also shown in Table 1. We find a slightly different set of parameters at $c = 0$ than reported by Sanchez and Lacombe, possibly because of some differences in which of the data points were included in the fit.

Our proposal is to examine whether the predictive or correlating capability of the Sanchez-Lacombe equation is improved by using any of the polyethylene parameter sets in Table 1 other than the set correlated without the volume shift.

Solvent Parameters

Sanchez-Lacombe parameters are available for ethylene [12] and for n-hexane [1]. These were regressed by least-squares fitting of selected vapor pressure and liquid density

data. Recently, we proposed obtaining solvent parameters from the critical temperature, critical pressure and the acentric factor [11]. Such data are available for many light components in Reid at al. [13]. The equation of state with these parameters reproduces the vapor pressures of ethylene and n-hexane over the reduced temperature range $0.7 \leq T_r \leq 1$ with maximum errors of 1.5% and 3.8%, respectively. The parameter sets are given in Table 2.

Correlation of Cloud Point Data

In correlating data, we have used a Newton-Raphson technique for generating the whole cloud-point curve rapidly, even when the polymer is characterized with many pseudo-components. The procedure is described by Koak [14] and by Koak and Heidemann [15]. It is an extension of phase boundary generation methods presented by Michelsen [16] and Nghiem and Li [17]. The availability of this method makes it possible to examine the effect of different parameterizations for the solvents and the polyethylene as well as the effect of the one binary interaction parameter.

The three sets of data examined were all obtained by measuring cloud-point temperatures and pressures for mixtures of fixed composition. We have referred to the de Loos and Kennis theses for the original data and have interpolated or extrapolated to produce isotherms covering the full range of the data. Calculations are compared to the isotherms.

The three polyethylenes differ in their average molar mass and polydispersity. The first (PE1) has mass average and number average molar masses of 99,000 and 56,000, respectively. The second (PE2) has mass average and number average molar masses of

8,800 and 7,600. It is, therefore, much lighter than the first and nearly monodisperse. Both of these polymers have been characterized with twelve pseudo-components using Hermitian quadrature to fit the number average molar mass, as described by Heidemann and Koak [18].

The polymer used by Kennis [5] for cloud-points with n-hexane had mass average and number average molar masses of with 177,000 and 8,000. This polymer was characterized with seven pseudo-components, again matching the number average molar mass through Hermitian quadrature. Because of the extreme polydispersity, the first two pseudo-components calculated had unrealistically low molar masses and they were discarded, leaving only five in the mixture. The Kennis [5] data include observations of liquid-liquid and vapor-liquid cloud points and of some three-phase points.

Correlation with Regressed Sanchez-Lacombe Parameters for the Solvents

The ethylene and n-hexane Sanchez-Lacombe parameters of Kiszka et al. [12] and Sanchez and Lacombe [1] were used (values are given in Table 2). If the Sanchez and Lacombe parameters for polyethylene are also used (see Table 1), it is possible to place the calculated cloud-point curves for PE1 over the experimental data with a temperature dependent interaction parameter. However, the critical point is at a low mole fraction compared with the data and the slopes of the calculated curves do not match the data.

It was found that the set of polyethylene parameters in Table 1 at $\varepsilon = 4950\,\text{J/mol}$ permitted a good match of both the slopes of the isotherms and the experimental critical point. A temperature dependent interaction parameter was required, with;

$$k_{ij} = -0.059425 + 0.000135\,T \tag{10}$$

In the temperature range of the data, this value is around -0.002.

Keeping the polyethylene parameter set for $\varepsilon = 4950 \, \text{J/mol}$, the cloud-point data for PE2 with ethylene and for PE3 with n-hexane were also fit by temperature dependent interaction parameters. The expressions are;

For PE2-ethylene; $\qquad\qquad k_{ij} = -0.061725 + 0.000135T$ $\qquad\qquad\qquad$ (11)

For PE3-n hexane; $\qquad\qquad k_{ij} = 0.012315 - 0.0001T$ $\qquad\qquad\qquad\qquad$ (12)

The results are shown in Figures 2 and 3. For PE2-ethylene, de Loos [3] reported experimental critical points at a polymer mass fraction of 0.162 ± 0.002. This value is reproduced by the calculations with good accuracy, as is the general shape of the cloud-point curves. The Kennis [5] data do not include an estimate of critical points, but do contain vapor-liquid cloud points and some three-phase points that are well reproduced by the calculations.

Correlation with Solvent Parameters from Critical Data

For many solvents, it may be most convenient to obtain the Sanchez-Lacombe parameters from the correlation against critical properties that was recently proposed by us [11]. The parameters for ethylene and n-hexane (see Table 2) were fixed in this manner and the polymer parameters and the polymer-solvent interaction parameters were again used to match cloud-point data.

The Kennis [5] data with n-hexane proved a challenge to fit with any interaction parameter unless the polymer parameters were chosen in a fairly narrow range of the values listed in Table 1. It was not possible to obtain a precise match of the PE1-ethylene critical mass fraction with any of the polymer parameter sets in this range. The compromise used

to obtain correlations of all three cloud-point systems was to take the polymer parameter set at $\varepsilon = 4600\,\text{J/mol}$. The interaction parameters required were again temperature dependent and are;

For PE1-ethylene; $\qquad\qquad k_{ij} = 0.149575 - 0.00005T$ $\qquad\qquad\qquad$ (13)

For PE2-ethylene; $\qquad\qquad k_{ij} = 0.19162 - 0.000064T$ $\qquad\qquad\qquad$ (14)

For PE3-n hexane; $\qquad\qquad k_{ij} = 0.07526 - 0.0004T$ $\qquad\qquad\qquad$ (15)

Results are shown in Figures 4 - 6.

As can be seen from Figures 4 and 5, the calculated critical mass fraction differs from the experimental value by about 0.02, so that certainly a parameter set for PE can be found which fits the critical points better. However, the slopes of the cloud-point curves for the systems PE1 + ethylene are captured very well by this parameter set for PE, which would not be the case for any other. Figure 6 displays a very good correlation of all the Kennis [5] data for PE3 and n-hexane.

Discussion

The calculations demonstrate that polyethylene solvent cloud-point behavior for a range of polymers and solvents can be correlated with the same set of polymer parameters. The use of a volume shift in fitting reference PVT data for polyethylene has made available a continuum of polymer parameters for data correlation purposes. Which of the sets of polymer parameters is best chosen would depend on which Sanchez-Lacombe parameters are used for the solvents involved.

The interaction parameters required are relatively small in magnitude. Unfortunately, the calculated results are extremely sensitive to these numbers, even in the

third figure after the decimal. Furthermore, temperature dependence, however slight, is essential in obtaining a match of data. The comment of Kirby and McHugh [19] that equations of state "can be used to correlate data, and, with caution, they can be used to simulate other experimental conditions not explicitly measured" applies to these results.

The pressures at which the de Loos [3, 4] and Kennis [5] data were measured range from 6 bar to nearly 2000 bar and the polymer mass fraction is generally below 0.2. Another range of experimental conditions where some data are available is at the polymer-rich, low pressure end where solvent volatility might be fitted by Henry's constants.

Table 3 shows the results of calculations using the correlations described above at a pressure of 1 atmosphere and temperatures where Maloney and Prausnitz [20] reported Henry's constants. The calculated ethylene in polyethylene Henry's constants are very close to the data, especially with the first of the correlations. Similar calculations for n-hexane in polyethylene are not as close to the data. The calculated Henry's constants are at conditions of pressure and composition far distant from the region where the correlation of cloud-points was performed and the temperature extends 130 $^{\circ}$C beyond any measurement.

Perhaps the close agreement with experimental equilibrium data at conditions extrapolated far from the conditions where the correlations were obtained must be regarded as merely fortuitous. However, it appears as if the first of the correlations for polyethylene with ethylene could be used over the whole range of conditions used in the manufacture of the polymer.

References

[1]   I.C. Sanchez, R.H. Lacombe, Statistical Thermodynamics of Polymer Solutions, Macromolecules, 11 (1978) 1145-1156

[2]   I.C. Sanchez, R.H. Lacombe, An Elementary Molecular Theory of Classical Fluids. Pure Fluids, J. Phys. Chem., 80 (1976) 2352-2362

[3]   Th.W. de Loos, W. Poot, G.A.M. Diepen, Fluid Phase Equilibria in the System Polyethylene + Ethylene. 1. Systems of Linear Polyethylene + Ethylene at High Pressures, Macromolecules, 16 (1983) 111-117

[4]   Th.W. de Loos, Evenwichten Tussen Fluïde Fasen in Systemen van Lineair Polyetheen en Etheen, Ph.D. Thesis, Delft Technical University, Delft, The Netherlands, 1981

[5]   H.A.J. Kennis, The Influence of Nitrogen on the Phase Behavior of the System n-Hexane/Linear High Density Polyethylene, M.Sc. Thesis, Delft Technical University, Delft, The Netherlands (1988)

[6]   H.A.J. Kennis, Th.W. de Loos, J. de Swaan Arons, R. van der Haegen, L. Kleintjens, The Influence of Nitrogen on the Liquid-Liquid Phase Behaviour of the System n-Hexane-Polyethylene: Experimental Results and Predictions with the Mean-Field Lattice-Gas Model, Chem. Engg Sci., 45 (1990) 1875-1884.

[7]   N. Koak, R.A. Heidemann, Polymer-Solvent Phase Behavior Near the Solvent Vapor Pressure, Ind. Eng. Chem. Res., 35 (1996) 4301-4309

[8]   I.C. Sanchez, R.H. Lacombe, An Elementary Equation of State for Polymer Liquids, J. Polymer Science, Part B: Polymer Letters, 15 (1977) 71-75

[9]   O. Olabisi, R. Simha, Pressure-Volume-Temperature Studies of Amorphous and Crystallizable Polymers. I. Experimental, Macromolecules, 8 (1975) 206-210

[10]   A. Peneloux, E. Rauzy, R.Freze, A Consistent Correlation for the Redlich-Kwong-Soave Volumes, Fluid Phase Equilibria, 8 (1982) 7-23

[11]   K. Gauter, R.A. Heidemann, A Proposal for Parametrizing the Sanchez-Lacombe Equation of State, Ind. Eng. Chem. Res., 39 (2000) 1115-1117.

[12]   M.B. Kiszka, M.A. Meilchen, M.A. McHugh, Modeling High-Pressure Gas-Polymer Mixtures Using the Sanchez-Lacombe Equation of State, J. Appl. Polym. Sci., 36 (1988) 583-597

[13]   R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, 4th Edition, McGraw-Hill, New York, 1988.

[14]   N. Koak, Polymer Solution Phase Behavior, Ph.D. Thesis, The University of Calgary, Calgary, Canada (1997)

[15]   N. Koak, R.A. Heidemann, Phase Boundary Calculations for Solutions of a Polydisperse Polymer, unpublished.

[16]   M.L. Michelsen, Calculation of Phase Envelopes and Critical Points in Multicomponent Mixtures, Fluid Phase Equilibria, 4 (1980) 1-10

[17]   L.X. Nghiem, Y.-K. Li, Computation of Multiphase Equilibrium Behavior with an Equation of State, Fluid Phase Equilibria, 17 (1984) 77-95

[18]   R.A Heidemann, N. Koak, letter to the Editor, AIChE J., 41 (1995) 737.

[19]   C.F. Kirby, M.A. McHugh, Phase Behavior of Polymers in Supercritical Fluid Solvents, 99 (1999) 565-602

[20]   D.P. Maloney, J.M. Prausnitz, Solubilities of Ethylene and Other Organic Solutes in Liquid, Low-Density Polyethylene in the Region 124°C to 300°C, AIChE J., 22 (1976) 74-82

Table 1. Equation of State Parameters for Polyethylene
Fit to Data of Olabisi and Simha [9]

ε, J/mol	v^* cm^3/mol	d/M_n, mol/g^{-1}	c, cm^3
5400	12.6078	0.09173	0.05711
5396.1**	12.6967**	0.0871**	
5300	12.2260	0.09068	0.01032
5200	11.8426	0.08967	-0.03540
5100	11.4577	0.08669	-0.08006
5000	11.0713	0.08776	-0.12369
4950	10.8776	0.08730	-0.14513
4900	10.6836	0.08686	-0.16632
4800	10.2945	0.08599	-0.20797
4700	9.9042	0.08517	-0.24868
4600	9.5127	0.08439	-0.28846
4500	9.1203	0.08366	-0.32733
4400	8.7271	0.08297	-0.36533
4300	8.3332	0.08232	-0.40247

** Fitting of Sanchez and Lacombe [1]

Table 2. Equation of State Parameters for Solvents

		ε, J/mol	v^* cm^3/mol	d
Ethylene	(regressed*)	2718.8	13.4165	4.059
Ethylene	(from critical data)	2288.5	7.4714	6.372
n-Hexane	(regressed**)	3957.7	13.2888	8.368
n-Hexane	(from critical data)	3684.8	12.5503	9.669

* Kiszka et al. [12]
** Sanchez and Lacombe [1]

Table 3. Henry's Constants from Sanchez-Lacombe Flash Calculations
Pressure in atmospheres, mass fraction solvent

	Polyethylene					n-Hexane		
	Data**	Calculated				Data**	Calculated	
T, ^{o}C		PE1(a)	PE1(b)	PE2(a)	PE2(b)		PE3(a)	PE3(b)
124	1390	1413	1772	1376	1544	20	11.2	6.2
150	1550	1617	1903	1577	1626	32.8	18.7	9.1
200	1830	1947	2079	1903	1728	67.7	40.0	16.2
250	2050	2174	2164	2128	1769	115	70	25.6
300	2260	2293	2173	2246	1764	176	105	36.9

** Maloney and Prausnitz [20]
(a)   Parameters from regression
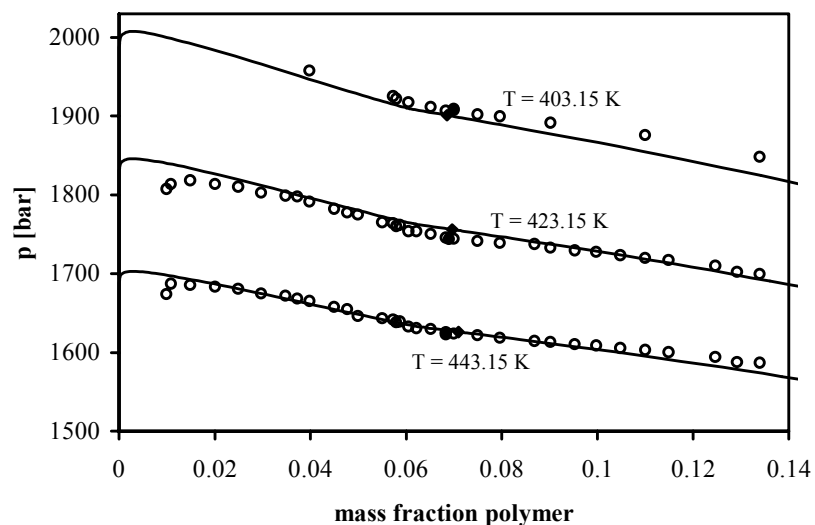(b)   Parameters from critical data [11]

Figure 1. Cloud Points; PE1 with Ethylene. Ethylene Parameters from Kiszka et al. [12].
Polyethylene Parameters from Table 1 with $\varepsilon = 4950$ J/mol. Interaction Parameter,
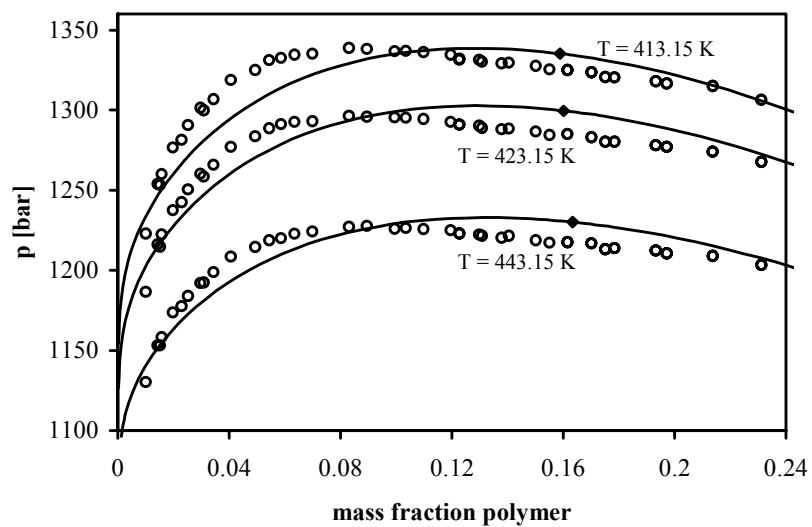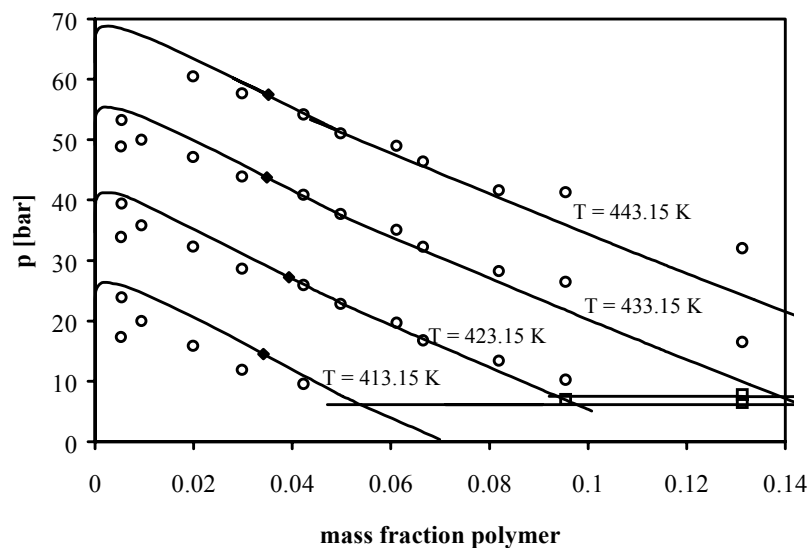$k_{ij} = -0.059425 + 0.000135T$

Figure 2. Cloud Points; PE2 with Ethylene. Ethylene Parameters from Kiszka et al. [12].
Polyethylene Parameters from Table 1 with $\varepsilon = 4950$ J/mol. Interaction Parameter,
$k_{ij} = -0.061725 + 0.000135T$

Fi gure 3.   Cloud Points; PE3 with n-Hexane. n-Hexane Parameters from Sanchez and Lacombe [1].   Polyethylene Parameters from Table 1 with ε = 4950 J/mol. Interaction Parameter, $k_{ij} = 0.012315 - 0.0001T$
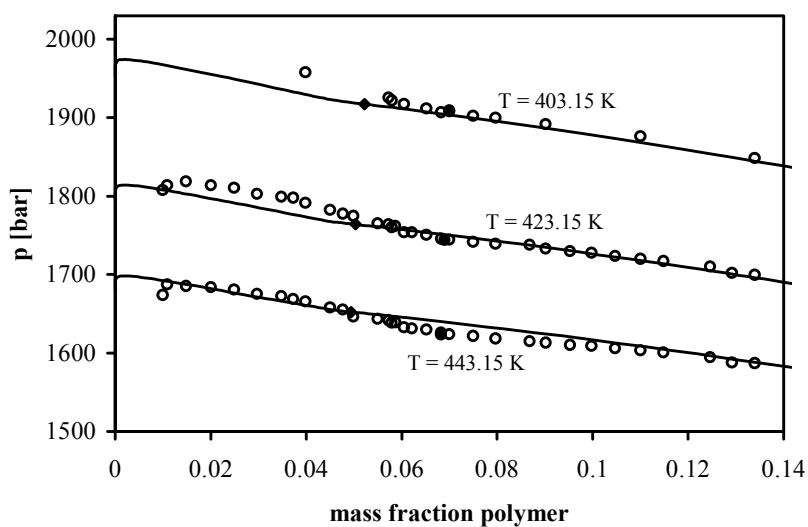

Figure 4. Cloud Points; PE1 with Ethylene. Ethylene Parameters from Critical Properties [11].   Polyethylene Parameters from Table 1 with ε = 4600 J/mol.   Interaction Parameter, $k_{ij} = 0.149575 - 0.00005T$
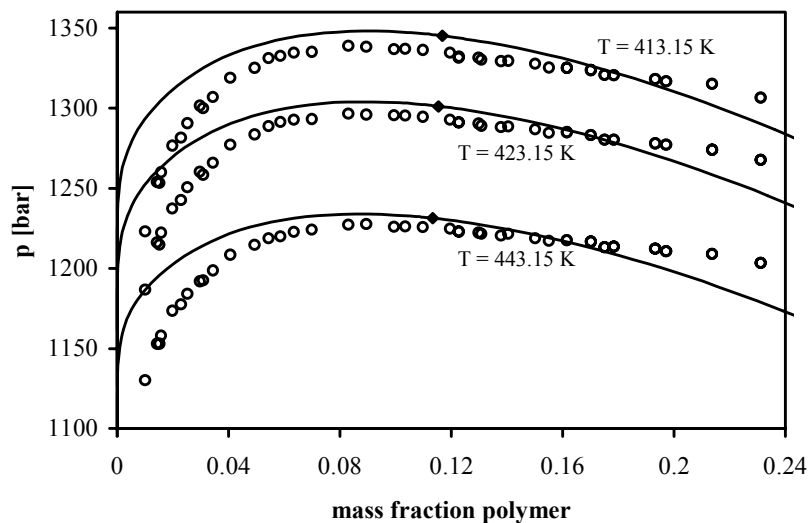
Figure 5. Cloud Points; PE2 with Ethylene. Ethylene Parameters from Critical Properties
[11]. Polyethylene Parameters from Table 1 with $\varepsilon = 4600$ J/mol. Interaction
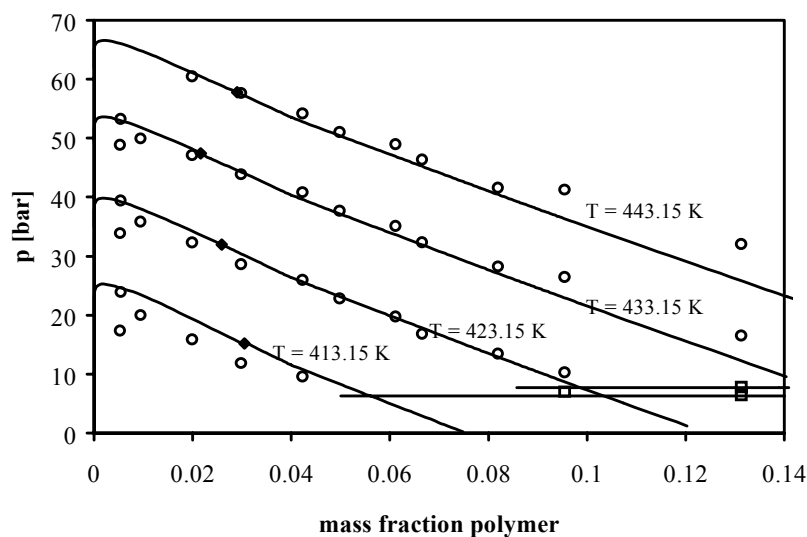Parameter, $k_{ij} = 0.19162 - 0.000064T$

Figure 6. Cloud Points; PE3 with n-Hexane. n-Hexane Parameters from Critical Properties
[11]. Polyethylene Parameters from Table 1 with $\varepsilon = 4600$ J/mol. Interaction
Parameter, $k_{ij} = 0.07526 - 0.0004T$